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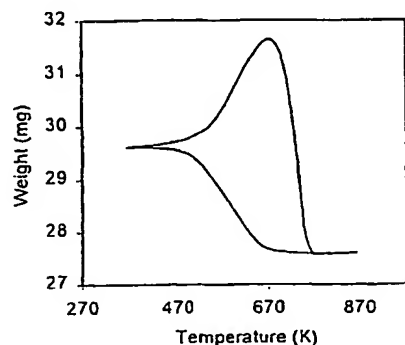
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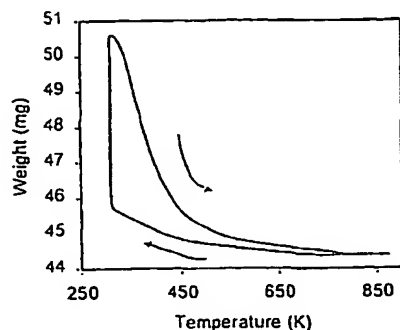
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- (71) Applicants (for all designated States except US): **NATIONAL UNIVERSITY OF SINGAPORE [SG/SG];**
10 Kent Ridge Crescent, Singapore 119260 (SG). **TAN, Kuang, Lee [SG/SG];** INTRO, National University of
- Singapore, 10 Kent Ridge Crescent, Singapore 119260 (SG).
- (71) Applicants and
(72) Inventors: **CHEN, Ping [CN/SG];** INTRO, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260 (SG). **LIN, Jianyi [SG/SG];** INTRO, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260 (SG).
- (74) Agent: **APPLIED RESEARCH CORPORATION;** Kent Ridge, P.O. Box 1016, Singapore 911101 (SG).
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(54) Title: **METHOD OF REVERSIBLY STORING H₂ AND H₂-STORAGE SYSTEM BASED ON METAL-DOPED CARBON-BASED MATERIALS**



(57) Abstract: This invention is directed to a method of reversibly storing hydrogen comprising exposing a solid sorbent of metal-doped carbon-based material to a hydrogen atmosphere at a temperature of from about 250 K to about 973 K under ambient or higher pressure. The metal-doped carbon-based material is generally an alkali metal-doped carbon-based material prepared by mixing a carbon material with an alkali metal salt and calcining the mixture under an atmosphere of inert or reductive gas.



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- 1 -

METHOD OF REVERSIBLY STORING H₂ AND H₂-STORAGE SYSTEM BASED ON METAL-DOPED CARBON-BASED MATERIALS

BACKGROUND OF THE INVENTION:

5 FIELD OF THE INVENTION:

This invention relates to a method of storing H₂ in metal-doped carbon-based solid state sorbents, such as carbon nanotubes (including stacked truncated carbon nanocones), carbon nanofibers, activated carbon, carbon fibers, graphite and amorphous carbon. The present invention also relates to metal-doped carbon-based sorbent materials capable of
10 absorbing up to 25 wt% of hydrogen at moderate temperature and pressure.

DESCRIPTION OF RELATED ART:

Hydrogen has been recognized as an ideal energy carrier. However, end-user hydrogen storage is still one of the challenging technical problems attracting increasing
15 research interest¹⁻⁵ to make it truly useful. In fact, a substantial number of research groups worldwide have put intensive effort to try to use a hydrogen based fuel cell as a power source for automobiles and other devices. These groups have encountered problems associated with high cost and low efficiency of the hydrogen storage systems.

Currently, there are four kinds of H₂ storage systems in use: (a) liquid hydrogen, (b)
20 compressed gas, (c) cryo-adsorption and (d) metal hydride storage systems. A brief description of these existing methods is given below:

(a) The liquid hydrogen storage system is of importance because it offers good solutions in terms of technology and economy, both for mobile storage systems and large-volume storage for volumes of from 100 litres to 5000 m³. However, in order to store the liquefied
25 hydrogen, the container (dewar) should be made of super-insulating materials, which is very expensive in practice.

(b) The compressed gas storage system is usually applied in underground supply systems, similar to a network of natural gas. This is an economical and simple method, but

- 2 -

it is unsafe and not portable.

(c) Cryo-adsorbing storage systems show advantages in moderate weight and volume. In this system, hydrogen molecules are bound to the sorbent only by physical adsorption forces, and remain in the gaseous state. The adsorbing temperature is in the range of 60 to 100 K. Normally, activated carbon is used as the sorbent due to its large portion of small pores serving as arenas for storing H₂. The efficiency of H₂ uptake is no more than 7 wt%, which is equivalent to about 20 kg H₂ per cubic meter of activated carbon. The disadvantages of this system relate to the low capacity and the much lower temperature required, which, similar to that of liquid hydrogen systems, makes it necessary to use suitable super-insulated containers, and thus the cost is increased.

(d) Metal hydride storage systems are recognized as a novel concept in hydrogen storage. These store large quantities of H₂ via a chemical reaction of $H + M = M-H$, wherein M is a selected metal system. Two major metal systems, i. e. Fe-Ti and Mg-Ni, have been applied as H₂ storage media and have been put into use in automobiles driven by an H₂/O₂ fuel cell. The operating temperature is 40 – 70°C for the Ti-Fe system and 250–350 °C for the Mg-Ni system. The H₂ storage capacity is less than 5 wt% for Ni-Mg and 2 wt% for Fe-Ti, which corresponds to less than 70 kg H₂ per cubic meter of metals. Furthermore, metal hydride systems normally require 20-40 bar pressure to keep the hydrogen in equilibrium. This renders the container for the metal hydride too heavy and expensive, and limits the practical exploitation of these systems.

The last two mentioned H₂ storage systems above are chosen only in some special applications due to their relatively low H₂ storage capacity and high cost. Embodiments of the present invention advantageously provide systems which increase H₂ storage capacity relative to prior systems and also provide for hydrogen storage under practical conditions.

Alkali-metal based materials have been reported as being able to absorb H₂. For Li-based materials, normally in the case of an Li battery, hydrogen absorption takes place under electro-chemical conditions¹. LiH can be formed at 300-500°C, but the dissociation requires 700-900°C. For K-based materials, it has been reported that about 160 ml of hydrogen was absorbed by 1 gram K-intercalated graphite at liquid nitrogen temperature⁶.

- 3 -

The intercalation of alkali metal into graphene layers may form a compound, C_nM .

More recently, several articles have been published^{7,8} concerning storing H_2 on carbon materials. A. C Dillon et al. reported that about 0.01 wt% of H_2 was absorbed by raw carbon nanotube material (which was estimated to constitute 5 wt% of the single wall nanotube material) at 130 K, and A. Chambers et al. reported 65 wt% of hydrogen uptake was achieved by using herringbone-like graphite nanofibers under 200 atm pressure.

BRIEF SUMMARY OF THE INVENTION:

The present invention advantageously provides a method which increases the hydrogen storage capacity of a solid sorbent. Advantageously, the present invention also provides a method which enables the storage of hydrogen to be reversibly performed under ambient or higher pressure and moderate temperature. Still further, the present invention advantageously provides a means to economically make an efficient sorbent.

The above advantages may be achieved by modifying the nature of a carbon-based material which is to be used as the sorbent in a hydrogen storage system. The modification according to the invention comprises the doping of the carbon-based material with a metal which doping causes a distinct change in the structural and electronic properties of the carbon-based material.

The terms "doping" and "doped", in the context of the description of the present invention, refers to the addition of metal to carbon materials with the result that the structural and electronic properties of the carbon material are changed. This contrasts with a more strict definition of doping where actual replacement of carbon atoms within the graphitic structure is assumed. Without being bound by any theory of the invention, the inventors believe that a carbon metal compound structure is formed.

According to one aspect of the invention, there is provided a method of reversibly storing hydrogen comprising exposing a solid sorbent of metal-doped carbon-based material to a hydrogen atmosphere at a temperature of from about 250 K to about 973 K under ambient or higher H_2 pressure, preferably from about 1 to about 200 atm, more preferably from about 1 to about 100 atm and most preferably from about 1 to about 5 atm.

- 4 -

According to another aspect of the invention, there is provided a method of reversibly storing hydrogen comprising pre-treatment of a solid sorbent comprising a metal-doped carbon-based material in an inert atmosphere at high temperature before exposing a solid sorbent of metal-doped carbon-based material to a hydrogen atmosphere at a lower temperature under ambient or higher H₂ pressure.

According to another aspect of the invention, there is provided a method of preparing an alkali metal-doped carbon-based material for use in reversibly storing hydrogen comprising mixing a carbon material with an alkali metal salt and calcining the mixture under an atmosphere of inert or reductive gases.

There is also provided a hydrogen storage system comprising an alkali metal-doped carbon-based material prepared in accordance with the method described in the immediately preceding paragraph.

Additional information concerning this invention is contained in P.Chen et al., Science 285 91 (1999), the entire contents of which are hereby incorporated by reference.

Additional features and advantages of the invention will be set forth in the description which follows, and in part will be apparent from the description, or may be learned by practice of the invention. These variations are considered to be in the scope of the invention. The objectives and other advantages of the invention will be realized and attained by the structure particularly pointed out in the written description and claims hereof as well as the appended drawings.

BRIEF DESCRIPTION OF THE DRAWINGS:

FIG. 1 is a thermogravimetric analysis (TGA) profile of a reversible H₂ sorption on Li-doped carbon nanotubes. The sample was pretreated at 873K for 1 h, then cooled to 300K, and heated up again to 873K.

FIG. 2 is a TGA profile of a reversible H₂ sorption on K-doped carbon nanotubes. The sample was pretreated at 873K for 1 h then cooled down to 298K, and kept at 298K for 2 h and was heated to 773K again.

- 5 -

FIGS. 3a-3d are schematic representations of various generic nanotube (FIGS. 3a, 3b and 3d) and nanofiber (FIG. 3c) structures. In (a) a single walled nanotube, in (b) a multi-walled nanotube, in (c) stacked nanocones and in (d) stacked truncated nanocones are illustrated.

5 FIGS. 4a-4d are schematic representations of the cross-sections of the nanotube (FIGS. 4a, 4b and 4d) and nanofiber (FIG. 4c) structures illustrated in FIGS. 3a-3d. In (a) a single walled nanotube, in (b) a multi-walled nanotube, in (c) stacked nanocones and in (d) stacked truncated nanocones are illustrated.

DETAILED DESCRIPTION OF THE INVENTION:

10 The alkali-doped carbon based materials are sensitive to oxygen or moisture. Exposure to oxygen during or after the calcination process greatly reduced the ability of the sorbent material to take up hydrogen. It is therefore preferred to use salt lacking oxygen in the calcination process. If the ability of hydrogen uptake of the alkali-doped carbon-based material is impaired by exposure to oxygen or moisture, this impairment can be reversed by
15 a pre-treatment at an elevated temperature for a period of time before charging the doped material with hydrogen.

Preferably the carbon material of the carbon-based material is selected from carbon nanotubes (including but not limited to stacked truncated carbon nanocones), activated carbon, carbon powder, amorphous or disordered carbon, carbon fibers, carbon nanofibers
20 and graphite, and the metal is an alkali metal.

Graphite is commercially available and has a layered structure, high crystallinity and low surface area. The typical graphite interplanar distance is 0.335 nm.

Carbon fibers are commercially available and made of carbon with a graphite-like structure. One way of making carbon fibers commercially is by catalytic decomposition of
25 hydrocarbons. The diameter of carbon fibers is on the order of microns up to centimeters.

Carbon nanofibers (or graphite nanofibers) are similar to carbon fibers in that they are made of carbon with a graphite-like structure⁸. However, the diameter is much smaller

- 6 -

in that it is on the order of nanometers. The smaller diameter may be related to the manufacturing process such as using a smaller sized catalyst⁹. Carbon fibers and carbon nanofibers have slender solid structure. One special type of carbon nanofiber structure is the so-called herringbone structure consisting of stacked nanocones (FIGS. 3c and 4c).

5 Carbon nanocones may be visualized as graphene sheets rolled into conical shells. When the conical shells are stacked up (FIG. 3c) they form nanofibers with so-called herringbone structures as shown in FIG. 4c. When the conical shells are truncated and are stacked up they form nanotubes as shown in FIG. 3d with a schematic cross-sectional representation as in FIG. 4d.

10 Active carbon is commercially available. The activity of activated carbon is related to its large surface area, porosity and low crystallinity.

Amorphous carbon is commercially available carbon with low crystallinity.

There are two types of carbon nanotubes referred to in this invention. The first type of carbon nanotubes has walls parallel to the longitudinal axis of the tubular structure. The walls have similar structure as that of graphite, but with graphene sheets arranged as nested concentric cylinders. These carbon nanotubes can be either single-wall (FIGS. 3a and 4a) or multi-wall (FIGS. 3b and 4b) depending on whether a single or multiple graphene sheets are arranged as nested concentric cylinders around each other. These carbon nanotubes can be made from catalytic disproportionation of CO, as previously reported¹⁰ or by other methods well known in the art. The outer diameter of these single- or multi-wall carbon nanotubes ranges from 1 to 35 nm with an average of 15 nm.

25 The second type of carbon nanotubes, the stacked truncated carbon nanocones, are made from CH₄ decomposition over the Ni-, Co- or Fe-based catalyst as previously reported¹⁰. The structure of stacked truncated carbon nanocones shows certain differences when compared with carbon nanotubes and graphite. For example, the truncated conical shells may be visualized as graphene sheets arranged into the shape of a frustum with open ends (FIG. 3d). The truncated conical shells pile up or stack up to form a hollow tubular shape with lengths varying from several microns up to several hundred microns. The outer diameter varies from 10 to 60 nm (average 30 nm) and the inner diameter varies from 0.1 to

- 7 -

10 nm depending on the conditions during catalytic decomposition of CH₄.

Preferably carbon nanotubes or nanofibers are used which have been prepared by catalytic disproportionation of CO (first type nanotube) or decomposition of CH₄ (second type nanotube) on a Ni-based catalyst. After purification, more than 75%, typically more than 85% and, more typically, 90% or more of the product is advantageously in the form of nanotubes. The structural properties of carbon nanotubes and nanofibers are similar to that of graphite, but with greater interlayer distance: 0.345 nm for both types of nanotubes, compared with 0.335 nm for graphite. Both nanotubes and nanofibers can reach several microns in length.

10 Most preferably, the nanotubes have the a stacked truncated nanocone structure as illustrated in FIG. 3d, a cross-sectional view of which appears in FIG. 4d.

Preferably, the metal-doped carbon-based material is an alkali metal-doped carbon-based material. The alkali metal may be, for example, Li, Na, K, Rb or Cs. Mixtures of alkali metals can be used. For example, two or three different metals can be used, preferably a mixture of Li and one additional alkali metal. An exemplary mixture is of Li and K.

In certain embodiments, the temperature for hydrogen absorption is in the range of 400-900 K for Li-doped carbon materials, preferably between 500 and 670 K, and 200-700 K for Na- or K-doped carbon materials, preferably between 300 and 470 K. The pressure for the absorption process is preferably as high as practical. The higher charging pressure results in saturation in a shorter time. Typically, the charging pressure is between 1 and 100 atm, more typically between 1 and 30 atm, most typically between 1 and 5 atm.

Figure 1 and 2 are the TGA spectra of Li-doped and K-doped carbon nanotubes, respectively, in the hydrogen uptake process. As shown in Figure 1, the Li-doped sample, prepared as in Example 2, was preheated in-situ at 873 K for 1 hour in a flow of purified hydrogen (99.99%) to remove absorbed water and contaminants, then gradually cooled down from 873 to 300 K and then heated up to 873 K again linearly (2 degrees/min). From Figure 1, it can be seen that the H₂ uptake began at temperatures around 772 K and ended at

- 8 -

423 K. When the temperature was increased again, the sample further increased its weight, reaching a maximum value at around 673 K. Further increasing the temperature resulted in the H₂ desorption, and the sample weight returned to its original value at 773 K. In Fig.2, the K-doped samples prepared in Example 4 were cooled down from 873 K to room temperature in an H₂ stream and remained so for 2 hours, then heated up again at 2 degrees/min to 873 K. A gradual weight increase was observed from 773 to 343 K (Figure 2). As the temperature was further decreased, a rapid weight increase occurred, reaching up to ~14 wt. % after the system was maintained at room temperature for 2 hours. Desorption of H₂ took place as the temperature was raised. The desorption was rapid between 300 and 423 K, and then became relatively gradual.

The doping of alkali metals to the carbon materials may be achieved by solid state reaction between the carbon materials and alkali metal salts. The solid state reaction method preferably involves thoroughly mixing the carbon materials with the alkali metal salt, then subjecting the mixture to high temperature treatment under inert gases, such as He, N₂, Ar, etc. or reductive gases such as H₂, etc.

The alkali-doped carbon based materials are sensitive to oxygen or moisture. Exposure to oxygen during or after the calcination process greatly reduces the ability of the sorbent material to take up hydrogen. It is therefore preferred to use a salt lacking in oxygen in the calcination process. If the ability of hydrogen uptake of the alkali-doped carbon-based material is impaired by exposure to oxygen or moisture, this impairment can be reversed by a pre-treatment at an elevated temperature under an inert atmosphere (e.g. Ar, N₂) or a reducing atmosphere (e.g. H₂) for a period of time before charging the doped material with hydrogen.

In certain embodiments, a pre-treatment at elevated temperature is performed on the doped material at temperatures ranging between 373 and 1073 K under an inert atmosphere such as Ar or N₂ before charging the doped material with H₂ at a lower temperature. For the K-doped material, the subrange between 573 and 973 K is typically chosen. For the Li-doped material, the subrange between 673 and 1023 K is typically chosen.

The alkali metal salts may include carbonates, nitrates, hydroxides, halogenides,

- 9 -

acetates, hydrides, nitrites, or the like. The molar ratio of alkali metal to the carbon materials in the reaction is preferably from about 1:50 to 1:1, more preferably from 1:10 to 1:1 for Li and 1:20 to 1:5 for K or Na.

More particularly, the temperature for the chemical reaction is preferably in the
5 range of from 473 to 1273 K according to the alkali metal salts selected. Typical conditions are 473-1073 K, more typically 773 to 1073 K for doping with Li under hydrogen or an inert gas, and 573-1273 K, more typically 623 to 973 K for doping with Na and K under hydrogen.

The abnormal capability for reversible H₂ sorption by the alkali metal-doped carbon
10 materials according to embodiments of the invention is derived from the doping of alkali metal into the carbon materials. The electronic structure of the carbon material is changed significantly due to the alkali metal doping, as revealed by our XPS and UPS studies. Alkali metal in the alkali metal-doped carbon-based materials transfers a near unity charge to carbon, resulting in an M⁺ state and a significant increase in free electron density in the
15 graphene layers. In the valence band region the alkali metal doping creates an extra density of states at the Fermi edge. This alkali metal-derived Fermi-level band shifts the Fermi level closer toward the instrument vacuum level and plays a particularly important role in reducing the activation energy for the dissociative hydrogen chemisorption. However, other mechanisms of reversible hydrogen sorption, such as physical adsorption, are possible.

20 The hydrogen dissociative absorption on carbon is a slow activated process, with an activation energy corresponding to an above-zero-energy crossing between the dissociated H-atoms and H₂ molecular potential curves. Few molecules may have high enough energy to surmount this intrinsic energy barrier, resulting in minimal sticking taking place on carbon at ambient pressure and moderate temperatures without metal-doping. Energetically
25 the key step for this process is the weakening and the final breaking of the H-H bond. Band-structure calculations indicate that the half-filled Fermi level band created by the alkali metal doping is formed by the hybridization of the alkali metal outermost s orbital with a low-lying bonding C π band. It has primarily a C π character, and is spatially confined near the C planes. This carbon metal band can overlap strongly with the hydrogen (1s²)* orbital,

- 10 -

resulting in the lowering and filling of this antibonding orbital, and hence the reduction of the activation energy for the hydrogen dissociative absorption. This results in enhanced hydrogen uptake on the alkali metal-doped carbon materials.

The cyclable hydrogen binding capacity of the alkali metal-doped carbon material of the invention is at least 5%, more preferably at least 15% of the weight of the unabsorbed material. More preferably, the cyclable hydrogen binding capacity is at least 20%, still more preferably up to 25% of the weight of the unabsorbed material, most preferably the cyclable capacity ranges from 20% to 25% of the weight of the unabsorbed alkali-doped carbon-based material.

The following specific examples are provided to illustrate the invention. It will be understood, however, that the specific details given in each example have been selected for purpose of illustration and are not to be construed as a limitation on the invention. Generally, the experiments were conducted under similar conditions for carbon sorbents doped with the same alkali metal, except for the selection of carbon materials and H₂ pressure.

Example 1

600 mg of stacked truncated carbon nanocones with average diameter of 30 nm were thoroughly mixed with 30 mol % LiI. The mixture was heated in a flow of purified helium at ambient pressure to 700°C and maintained for 1h, and then cooled to room temperature to form Li-doped stacked truncated carbon nanocones. 30 mg of Li-doped stacked truncated carbon nanocones were put into the sample holder of a thermogravimetric analyzer (TGA), and H₂ was introduced as the purging and holding gas. After maintaining the sample at room temperature for 60 min and purging with H₂, maintaining an H₂ atmosphere at 30 psi to drive away the air left in the sample chamber, the temperature was increased from room temperature to 973K at a rate of 20 K/min, and maintained at 973K for 1 h to outgas the absorbed water and volatile contaminants. Then, the sample was cooled to 623K at a rate of 20 K/min, and maintained for 2 h. A weight increase of 20 % due to hydrogen uptake was achieved after this process.

- 11 -

Example 2

600 mg of carbon nanotubes were mixed with 20 mol % LiNO_3 . The mixture was heated to 800°C and maintained for half an hour, and then cooled to room temperature to form Li-doped carbon nanotubes. Using 20 mg of the prepared Li-doped carbon nanotubes and putting into the sample holder of the TGA, and following the same procedures as example 1, a weight increase of 10 % was achieved.

Example 3

Using graphite as the starting material and following the same procedures of example 1, a weight increase of 12 % was achieved.

10

Example 4

600 mg of activated carbon was mixed with 30 mol % of KOH. The mixture was calcined at 800°C for half an hour in a flow of purified hydrogen, and then cooled to room temperature to form K-doped activated carbon. 50 mg of K-doped activated carbon was put in the sample container of the TGA, and purified H_2 was introduced to the TGA system as the purge gas. The system was heated to 873K to remove absorbed water and volatile contaminants, and then cooled to 298K and maintained for 2 h. A weight increase of about 14 % was achieved (Fig.2).

Example 5

Using stacked truncated carbon nanocones as the starting material and following the same procedures of example 4, a weight increase of 14 % was obtained.

Example 6

600 mg of activated carbon was mixed with 2 molar % of KOH. The mixture was calcined at 400°C for an hour in a flow of purified hydrogen, and then cooled down to room temperature to form K-doped activated carbon. 50 mg of K-doped activated carbon was put

- 12 -

in the sample container of the TGA, and purified H₂ was introduced as the purge gas to the TGA system. The system was heated to 673K to remove absorbed water and volatile contaminants, and then cooled down to 298K and maintained for 2 h. A weight increase of about 5 % was achieved after such a process.

5

Example 7

Using NaOH and activated carbon as the starting material and following the same procedures of example 4, a weight increase of about 13 % was achieved.

Example 8

Using Li-doped stacked truncated carbon nanocones as the sorbent, and exposing to
10 purified H₂ at 200 psi, a weight increase of 20 % was achieved within 1 h. This is shorter than the 2 h required for the similar test in example 1.

Example 9

Using Li-doped carbon nanotubes (multi-wall, first type nanotubes) as the sorbent, then following the same procedures of example 1, a weight increase of 15 % was achieved.

15

Example 10

100 mg of Ni catalyst was pre-reduced at 700°C in a flow of purified hydrogen in a tubular reactor for 1 hour. The hydrogen gas was then replaced by purified CH₄ as the feed-gas and the reaction system was maintained at 700°C for 1 hour to let CH₄ decompose on the Ni catalyst. The CH₄ gas supply was then turned off and the catalyst together with
20 the material formed was allowed to cool down to room temperature under ambient pressure. The material collected comprises truncated stacked carbon nanocones with metal catalyst attached, formed by decomposition of CH₄ on the Ni catalyst.

The material collected is then washed in dilute nitric acid and rinsed with distilled water to remove the attached metal catalyst. 600 mg of the stacked truncated nanocones

- 13 -

thus derived was thoroughly mixed with 50 molar % LiI and, following the same procedure as in Example 1, a weight increase of 25% was observed.

The H₂-rechargeability of Li- and K-doped samples was tested by TGA. For Li-doped samples (carbon nanotubes and graphite), the saturated H₂ uptake was measured at
5 653K after each complete desorption at 823 K, whereas for K-doped carbon materials it was measured at 298 K after each run of desorption at 773 K. The results show that after more than 20 cycles of absorption-desorption, the capacities of H₂ uptake are reduced by less than 10% for both systems.

To those skilled in the art, it is to be understood that many changes, modifications
10 and variations could be made without departing from the spirit and scope of the present invention. The disclosures and the descriptions herein are purely illustrative and are not intended to limit the scope of the invention, which is defined and by the claims.

References:

1. G. C. Carter and F. L. Carter. *Metal-Hydrogen Systems*. T. Nejat Veziroglu, Eds. (Pergamon, Oxford, 1981). chap. 7.
2. H. Buchner, P. Pelloux-Gervais, M. Müller, F. Grafwallner and P. Luger. *Hydrogen and other alternative fuels for air and ground transportation*. H. W. Pohl, Eds. (John Wiley & Sons, Chichester 1995). chaps. 7-11.
3. J. Nitsch, W. Peschka, W. Schnurnberger, M. Fischer and H. Eichert. *Hydrogen as an energy carrier*. C. Winter and J. Nitsch, Eds. (Springer-Verlag, Berlin, 1988). part B.
4. S. Hynek, W. Füller and J. Bentley. *Int. J. Hydrogen Energy*, **22**, 601 (1997).
5. J. S. Noh, R. K. Agarwal and J. A. Schwarz, *Int. J. Hydrogen Energy*, **12**, 693 (1987).
6. K. Watanabe, M. Soma, T. Onishi and K. Tamaru. *Nature*, **233**, 160 (1971).
7. A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune and M. J. Heben. *Nature*, **386**, 377 (1997).
8. A. Chambers, C. Park and R. T. K. Baker. *J. Phys. Chem. B*, **102**, 4253 (1998).
9. N.M. Rodriguez, *J. Mater. Res.*, **8** (12) 3233 (1993)
10. P. Chen et al. *Carbon* **35** (Bi, 10-11) 1495 (1997)
11. V.A. Nalimova et al. *Synthetic Metals*, **88** 89 (1997)

CLAIMS:

- 1 1. A method of reversibly storing hydrogen comprising exposing a solid sorbent
2 comprising a metal-doped carbon-based material to a hydrogen atmosphere at a temperature
3 of from about 200 K to about 973 K under 1 atm or higher H₂ pressure.
- 1 2. The method of claim 1, wherein the metal-doped carbon-based material is a
2 carbon-based material doped with at least one alkali metal.
- 1 3. The method of claim 2, wherein the at least one alkali metal is selected from the
2 group consisting of Li, Na, K, Rb and Cs.
- 1 4. The method of claim 2, wherein the alkali metal is Li and the solid sorbent is
2 exposed to said hydrogen atmosphere at a temperature of from 400 to 900 K.
- 1 5. The method of claim 2, wherein the alkali metal is Na or K and the solid sorbent
2 is exposed to the hydrogen atmosphere at a temperature of from 200 to 700 K.
- 1 6. The method of claim 2, wherein the alkali metal-doped carbon-based material is
2 doped with a mixture of more than one alkali metal.
- 1 7. The method of claim 6, wherein the mixture of more than one alkali metal
2 comprises Li and at least one other alkali metal.
- 1 8. The method of claim 7, wherein the mixture of more than one alkali metal
2 comprises Li and K.
- 1 9. The method of claim 2, wherein the alkali metal-doped carbon-based material is
2 prepared by a solid state reaction between at least one carbon material and at least one alkali
3 metal salt wherein the solid state reaction comprises mixing the at least one alkali metal salt
4 and the at least one carbon material, and calcining the mixture under an atmosphere of inert
5 or reductive gas.

1 10. The method of claim 9, wherein the alkali metal salt is one or more selected
2 from the group consisting of nitrates, hydroxides, carbonates, halogenides, acetates,
3 hydrides and nitrites.

1 11. The method of claim 9, wherein the carbon material consists of graphite and the
2 alkali metal salt consists of Li-halogenide.

1 12. The method of claim 9, wherein the carbon material consist of activated carbon
2 and the alkali metal salt is either K- or Na-hydroxide.

1 13. The method of claim 9, wherein the alkali metal salt is mixed with the carbon
2 based material in a molar ratio of alkali metal to the carbon material from 1:50 to 1:1 in the
3 reaction.

1 14. The method of claim 13, wherein the molar ratio of alkali metal to carbon is 1:2
2 in the reaction.

1 15. The method of claim 14, wherein the alkali metal is Li.

1 16. The method of claim 9, wherein the alkali metal salt is an Li salt and the chemical
2 reaction is carried out at a temperature of from 573 to 1073 K under a hydrogen or inert gas
3 atmosphere or wherein the alkali metal salt is a Na or K salt and the chemical reaction is
4 carried out at a temperature of from 573 to 1273 K under a hydrogen atmosphere.

1 17. The method of claim 1, wherein the solid sorbent is exposed to the hydrogen
2 atmosphere at a pressure of from 1 to 200 atm.

1 18. The method of claim 1, wherein said metal-doped carbon-based material
2 comprises at least one carbon material selected from the group comprising carbon fibers,
3 carbon nanofibers, activated carbon, carbon nanotubes, graphite and amorphous carbon.

1 19. The method of claim 18, wherein the carbon material consists of stacked
2 truncated nanocone type nanotubes.

1 20. The method of claim 18, wherein the carbon material comprises either carbon
2 nanotubes with single or multiple walls having an average outer diameter of 1 to 35 nm or
3 stacked truncated nanocones having an average outer diameter of 10 to 60 nm.

1 21. A method of reversibly storing hydrogen comprising:
2 pre-treating a solid sorbent comprising a metal-doped carbon-based material in an
3 inert atmosphere; and
4 exposing the solid sorbent to a hydrogen atmosphere at a temperature of from 200 K
5 to 973 K under ambient or higher H₂ pressure.

1 22. The method of claim 21, wherein the pre-treating step is carried out at between
2 373 and 1073 K.

1 23. A material prepared according to the method of claim 21, wherein the hydrogen
2 storage capacity is up to 25 wt %.

1 24. The material of claim 23, wherein the hydrogen storage capacity is up to 20
2 wt. %.

1 25. The alkali doped stacked truncated nanocone material of claim 24, having a
2 capacity of binding up to 20 wt. % of hydrogen.

1 26. A hydrogen storage system comprising the alkali metal doped carbon-based
2 material prepared in accordance with the method of claim 21.

1 27. The system of claim 26 wherein the hydrogen storage capacity is up to 25 wt. %
2 and there is rechargeability of at least 90% after 20 cycles of absorption-desorption.

1 28. The system of claim 27, wherein the hydrogen storage capacity is between 20
2 and 25 wt. %.

1 29. The method of claim 21, wherein the metal-doped carbon-based material is an
2 alkali metal-doped carbon-based material.

1 30. The method of claim 29, wherein the alkali metal is Li and the solid sorbent is
2 exposed to the hydrogen atmosphere at a temperature of from 400 to 900 K.

1 31. The method of claim 29, wherein the alkali metal is Na or K and the solid
2 sorbent is exposed to the hydrogen atmosphere at a temperature of from 200 to 700 K.

1 32. The method of claim 29, wherein the alkali metal-doped carbon-based material
2 is prepared by a solid state reaction between the carbon material and at least one alkali metal
3 salt and wherein the chemical reaction comprises mixing the alkali metal salt and the carbon
4 material, and calcining the mixture under an atmosphere of inert or reductive gas.

1 33. The method of claim 32, wherein the alkali metal salt is one or more selected
2 from the group consisting of nitrates, hydroxides, carbonates, halogenides, acetates,
3 hydrides, and nitrites and wherein the molar ratio of alkali metal to carbon in said alkali
4 metal-doped carbon-based material is from 1:50 to 1:1 in the reaction.

1 34. The method of claim 32, wherein the carbon material consists of graphite and
2 the alkali metal salt consists of Li-halogenide.

1 35. The method of claim 32, wherein the carbon material consist of activated
2 carbon and the alkali metal salt is either K- or Na-hydroxide.

1 36. The method of claim 32, wherein the alkali metal salt is a Li salt and the
2 chemical reaction is carried out at a temperature of from 573 to 1073 K under a hydrogen
3 or inert gas atmosphere or wherein the alkali metal salt is a Na or K salt and the chemical
4 reaction is carried out at a temperature of from 573 to 1273 K under a hydrogen
5 atmosphere.

1 37. The method of claim 21, wherein the solid sorbent is exposed to the hydrogen
2 atmosphere at a pressure of from 1 to 200 atm.

1 38. The method of claim 21, wherein the metal-doped carbon-based material
2 comprises at least one carbon material selected from the group consisting of carbon fibers,
3 carbon nanofibers, activated carbon, carbon nanotubes, graphite and amorphous carbon.

1 39. The method of claim 38, wherein the carbon material comprises either carbon
2 nanotubes with single or multiple walls having an average outer diameter of 1 to 35 nm or
3 stacked truncated carbon nanocones having an average outer diameter of 10 to 60 nm.

1 40. An alkali-metal doped, stacked truncated nanocone material having a capacity of
2 binding up to 25 wt. %, based on the mass of the alkali-metal doped nanocones material, of
3 hydrogen at an H₂ pressure of about 1 atm.

1 41. A method for preparing an alkali-metal doped stacked truncated carbon nanocone
2 material comprising:

3 heating a reduced Ni, Co or Fe catalyst in CH₄ to form a stacked truncated carbon
4 nanocone material;

5 mixing the truncated stacked carbon nanocone material with at least one alkali metal
6 salt; and

7 heating the mixture under an inert or reductive gas atmosphere to obtain an alkali-
8 metal doped truncated stacked nanocone material.

1 42. The method of claim 41, further comprising:

2 removing the metal catalyst from the stacked truncated carbon nanocone material by
3 washing the stacked truncated carbon nanocones in dilute acid.

1 43. The method of claim 41, wherein the at least one alkali metal salt is a
2 halogenide salt.

1 44. The method of claim 41, wherein a single alkali metal salt is used.

1 45. The method of claim 41 further comprising:

2 cooling the alkali-metal doped stacked truncated carbon nanocone material to room
3 temperature; and

4 heating the alkali-metal doped stacked truncated carbon nanocone material to a
5 temperature of 373 to 1073 K under an inert or reductive gas atmosphere.

1 46. An alkali metal doped stacked truncated carbon nanocone material prepared by
2 the process of claim 41.

1 47. A method for preparing an alkali-metal doped graphite comprising:

2 mixing graphite with at least one alkali metal salt; and

3 heating the mixture under an inert or reductive gas atmosphere to obtain an alkali-
4 metal doped graphite.

1 48. A method for preparing an alkali-metal doped activated carbon comprising:

2 mixing activated carbon with at least one alkali metal salt; and

3 heating the mixture under an inert or reductive gas atmosphere to obtain an alkali-
4 metal doped activated carbon.

1 49. A method of preparing an alkali metal-doped carbon-based material for use in
2 reversibly storing hydrogen comprising mixing a carbon material with an alkali metal salt
3 and calcining the mixture under an atmosphere of inert or reductive gas.

1 50. The method of claim 49, wherein the chemical reaction is carried out under a
2 He, N₂, Ar or H₂ atmosphere.

1 51. The method of claim 49, wherein the alkali metal salt is a nitrate, hydroxide,
2 carbonate, halogenide, acetate hydride, nitrite or the like.

1 52. The method of claim 49, wherein the molar ratio of alkali metal to carbon is
2 from 1:50 to 1:1.

1 53. The method of claim 49, wherein the alkali metal salt is a Li salt and the
2 chemical reaction is carried out at a temperature of from 573 to 1073 K under a hydrogen or
3 inert gas atmosphere.

1 54. The method of claim 49, wherein the alkali metal salt is a Na or K salt and the
2 chemical reaction is carried out at a temperature of from 573 to 1273 K under a hydrogen
3 atmosphere.

1 55. The method of claim 49, wherein the carbon material is selected from carbon
2 fiber, carbon nanofiber, activated carbon, carbon nanotubes, graphite and amorphous
3 carbon.

1 56. The method of claim 55, wherein the carbon material comprises carbon
2 nanotubes having an average diameter of 1 to 35 nm.

1 57. The method of claim 55, wherein the carbon material comprises stacked
2 truncated carbon nanocones having an average diameter of 10 to 60 nm.

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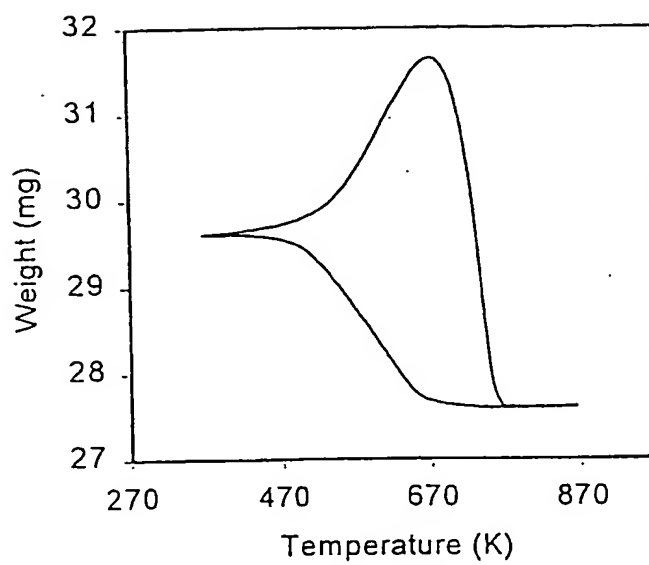


Fig. 1

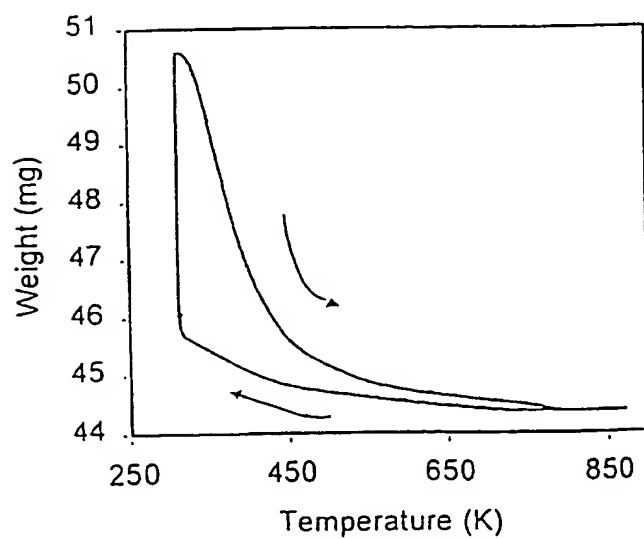
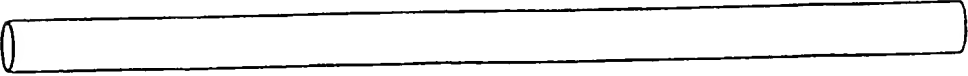

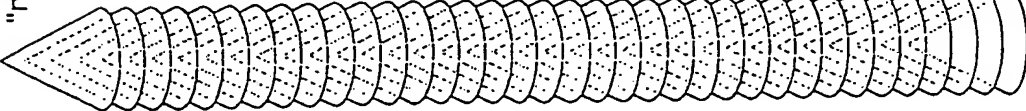
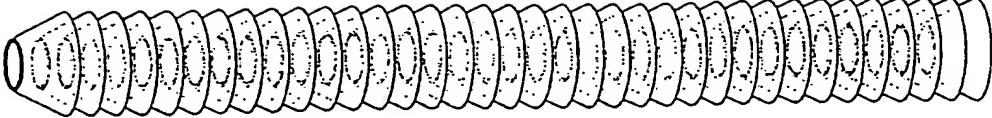
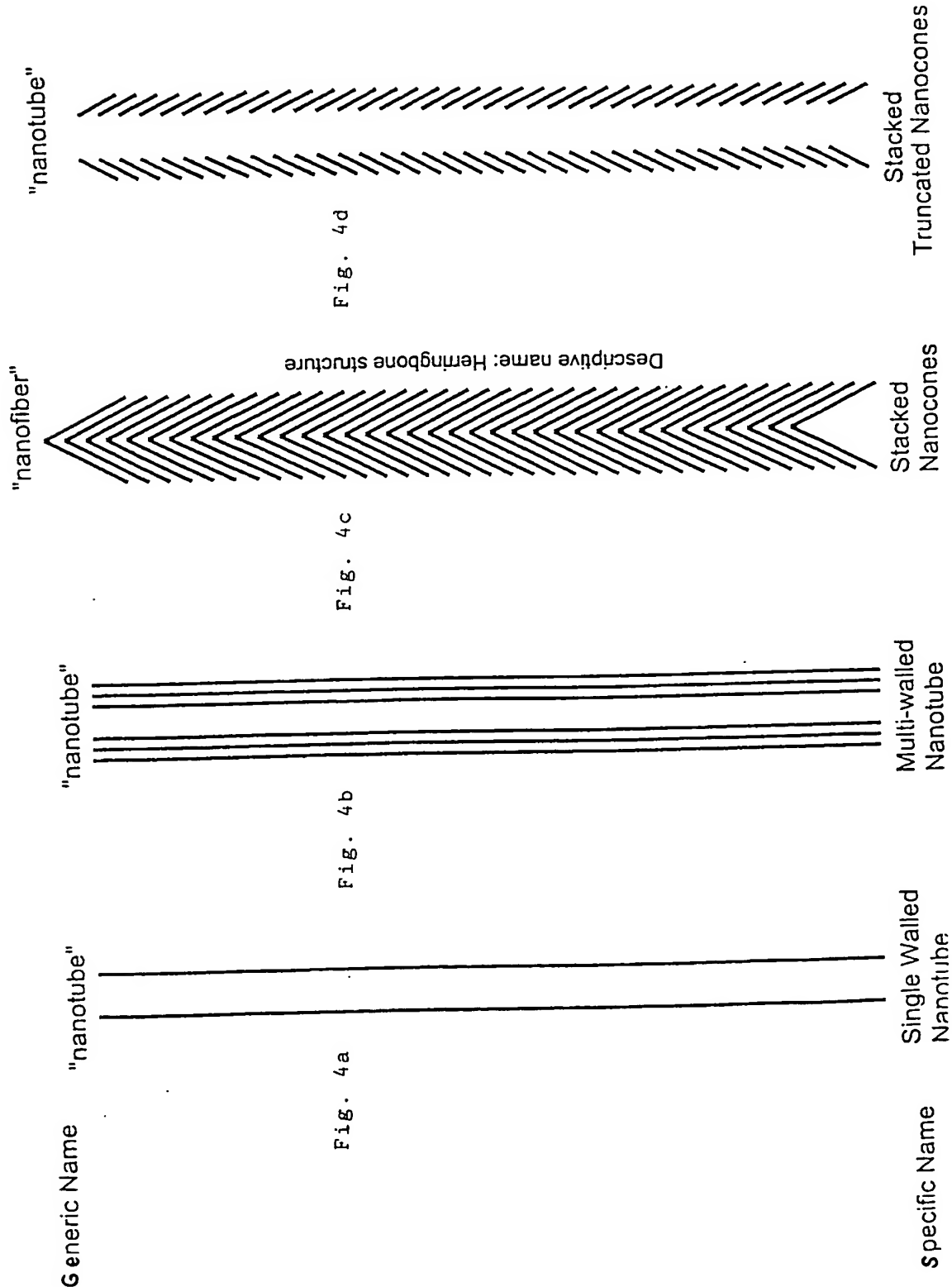


Fig. 2

Generic Name			Specific Name
"nanotube"		Fig. 3a	Single Walled Nanotube
"nanotube"		Fig. 3b	Multi-walled Nanotube
"nanofiber"		Fig. 3c	Stacked Nanocones
"nanotube"		Fig. 3d	Stacked Truncated Nanocones



INTERNATIONAL SEARCH REPORT

International application No
PCT/SG 00/00058

CLASSIFICATION OF SUBJECT MATTER		
IPC ⁷ : F 17 C 11/00; B 01 J 20/20; C 01 B 3/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
IPC ⁷ : F 17 C; B 01 J; C 01 B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
WPIL		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 19745549 A1 (MANNESMANN AG) 15 April 1999 (15.04.99) totality.	1.9.10.17- 28.32.41-51
A		2-8.11-16.29- 31.33-40.52-57
A	EP 0112548 A1 (STUDIENGESELLSCHAFT KOHLE) 4 July 1987 (04.07.87) claims.	1-57

<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/SG 00/00058

Patent document cited in search report			Publication date	Patent family member(s)			Publication date
DE	A1	19745549	15-04-1999	AU	A1	15543/99	03-05-1999
DE	C2	15745549	04-11-1999	WO	A2	9919253	22-04-1999
				WO	A3	9919253	24-06-1999
EP	A2	112548	04-07-1984	AT	E	46305	15-09-1989
EP	A3	112548	18-03-1987	AT	E	77602	15-07-1992
EP	B1	112548	13-09-1989	AU	A1	22754/83	28-06-1984
				AU	B2	568524	07-01-1988
				CA	A1	1225077	04-08-1987
				CA	A2	1233157	23-02-1988
				DE	A1	3247360	05-07-1984
				DE	C0	3380559	19-10-1989
				DE	C0	3382583	30-07-1992
				DK	A0	5922/83	19-12-1983
				DK	A	5922/83	23-06-1984
				DK	A	1457/91	12-08-1991
				DK	A0	1457/91	12-08-1991
				DK	B	162760	09-12-1991
				DK	C	162760	27-04-1992
				EP	A2	316968	24-05-1989
				EP	A3	316968	25-07-1990
				EP	B1	316968	24-06-1992
				ES	A1	528244	01-08-1984
				ES	A5	528244	31-08-1984
				ES	A1	8406371	01-11-1984
				IE	B	58010	16-06-1993
				IE	B	58026	16-06-1993
				JP	A2	59174501	03-10-1984
				US	A	4554152	19-11-1985
				US	A	4798718	17-01-1989
				US	A	5162108	10-11-1992
				US	A	5199972	06-04-1993
				US	A	4554153	19-11-1985
				US	A	4695446	22-09-1987
				US	A	4749558	07-06-1988
				US	A	5069894	03-12-1991
				US	A	4957727	18-09-1990
				AT	A	738/79	15-09-1985
				AT	B	380223	25-04-1986
				AU	A1	43880/79	09-08-1979
				AU	B2	526947	10-02-1983
				BR	A	7900628	28-08-1979
				CA	A1	1135480	16-11-1982
				DD	C	141297	23-04-1980
				DE	A1	2804445	09-08-1979
				DE	C0	2962411	19-05-1982
				DK	A	444/79	03-08-1979
				DK	B	151374	30-11-1987
				DK	C	151374	13-06-1988
				EP	A1	3564	22-08-1979
				EP	B1	3564	07-04-1982
				ES	A1	477378	01-07-1979
				ES	A5	477378	20-07-1979
				IE	B	48062	19-09-1984
				IL	A1	56562	30-04-1982
				JP	A2	54112799	03-09-1979
				JP	B4	63046001	13-09-1988
				MX	A	151049	18-09-1984
				SU	A3	1109047	15-08-1984
				AT	E	40667	15-02-1989
				AU	A1	22756/83	28-06-1984
				AU	B2	574056	30-06-1988
				CA	A1	1241181	30-08-1988
				DE	A1	3247361	28-06-1984
				DE	C0	3379164	16-03-1989
				DK	A0	5904/83	19-12-1983
				DK	A	5904/83	23-06-1984
				DK	B	162634	25-11-1991
				DK	C	162634	13-04-1992
				EP	A2	111923	27-06-1984
				EP	A3	111923	23-07-1986
				EP	B1	111923	08-02-1989
				ES	A1	528245	01-08-1984
				ES	A5	528245	31-08-1984
				ES	A1	8406372	01-11-1984
				IE	B	56386	17-07-1991

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/SG 00/00058

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		JP A2 59131503	28-07-1984
		JP B4 5009364	04-02-1993
		AT E 40573	15-02-1989
		AU A1 35230/84	30-05-1985
		AU B2 575354	28-07-1988
		CA A1 1232764	16-02-1988
		CA A2 1240156	09-08-1988
		DD A5 229157	30-10-1985
		DE A1 3340492	15-05-1985
		DE C0 3476561	09-03-1989
		DK A0 5232/84	02-11-1984
		DK A 5232/84	10-05-1985
		DK B 164368	15-06-1992
		DK C 164368	02-11-1992
		EP A1 147581	10-07-1985
		EP B1 147581	01-02-1989
		ES A1 537364	16-09-1985
		ES A5 537364	16-10-1985
		ES A1 8600418	01-01-1986
		IE B 57704	10-03-1993
		JP A2 60116732	24-06-1985
		JP B4 3031773	08-05-1991
		US A 4659373	21-04-1987
		US A 4731203	15-03-1988

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